Effect of linear and non-linear components in the temperature dependences of thermoelectric properties on the energy conversion efficiency

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ABSTRACT

The new thermal rate equations were built up by taking the linear and non-linear components in the temperature dependences of the Seebeck coefficient α, the electrical resistivity ρ and thermal conductivity κ of a thermoelectric (TE) material into the thermal rate equations on the assumption that their temperature dependences are expressed by a quadratic function of temperature T. The energy conversion efficiency η for a single TE element was formulated using the new thermal rate ones proposed here. By applying it to the high-performance half-Heusler compound, the non-linear component in the temperature dependence of α among those of the TE properties has the greatest effect on η, so that η/η_0 was increased by 11% under the condition of $T = 510$ K and $\Delta T = 440$ K, where η_0 is a well-known conventional energy conversion efficiency. It was thus found that the temperature dependences of TE properties have a significant influence on η. When one evaluates the accurate achievement rate of η_{exp} obtained experimentally for a TE generator, therefore, η_{exp} should be compared with η_{the} estimated from the theoretical expression proposed here, not with η_0, particularly when there is a strong non-linearity in the temperature dependence of TE properties.

1. Introduction

There has been considerable interest during the past 10 years in finding new materials and structures for use in clear, highly efficient cooling and energy conversion systems [1,2]. The thermoelectric (TE) figure of merit ZT provides a measure of the quality of such materials for applications and is defined as $ZT = \alpha^2 T/\rho\kappa$, where α is the Seebeck coefficient, ρ is the electrical resistivity, κ is the thermal conductivity and T is the absolute temperature [1]. The increase in ZT leads directly to the improvement in the energy conversion efficiency of TE generators and in the cooling efficiency of Pelteir modules [3]. Much effort has been made to raise ZT of TE bulk materials for the improvement of energy conversion efficiency and there were indeed some improvements in ZT (for example, $\sim$2 at 700 K for the p-type TAGS (GeTe–AgSbTe$_2$) [4], about 1.5 at 700 K for the n-type (Zr-Hf)NiSn half-Heusler compound [5]) and $\sim$2.2 at 800 K for the n-type AgPb$_{18}$SbTe$_{20}$ [6], but even their values are not sufficient to improve dramatically the energy conversion efficiency.

The energy conversion efficiency η has been derived analytically using the well-known thermal rate equations at the cold and hot junctions of a TE element [3,7]. The linear change in α with temperature has been taken into the conventional thermal rate equations

by Ioffe [7] and the linear changes in α, ρ and κ with temperature were recently taken into them by us [8]. However, the non-linear components in the temperature dependences of the TE properties have been neglected in the thermal rate equations, although generally they vary non-linearly with changes in temperature along a TE element. The traditional expression for η obtained from the conventional thermal rate equations should thus be not correct exactly. From this reason, η has been calculated numerically by solving the differential equations governing TE properties by the software tool in which the correct temperature dependence of TE properties is taken into account [9]. However, such a calculation has never clarified analytically the degree to which each temperature dependence of TE properties has an effect on η. To make it clear, we made an attempt to take the difference between the TE properties at the hot and cold sides of a TE element into the thermal rate equations on the assumption that all of the TE properties are expressed by a quadratic function of temperature. The new thermal rate equations were thus formulated by taking both the linear and non-linear components in the temperature dependences of TE properties into the thermal rate equations. The reason that the expression of η/η_0 derived here was applied to the half-Heusler compound [5] is that the temperature dependences of its TE properties are expressed well by a quadratic function of temperature and its compound has an excellent ZT, where η and η_0 are the energy conversion efficiencies calculated using the new and the conventional thermal equations, respectively. η was then derived

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Nomenclature

TE	thermoelectric
Z	thermoelectric figure of merit (K^{-1})
ZT	dimensionless thermoelectric figure of merit
T	mean temperature of a TE element (given by $T = (T_h + T_c)/2$) (K)
ΔT	temperature difference between both ends of a TE element (K)
T_z	temperature at a position z of a TE element (K)
T_h	temperature at the hot junction of a TE element (given by $T + \Delta T/2$) (K)
T_c	temperature at the cold junction of a TE element (given by $T - \Delta T/2$) (K)
$K(T)$	thermal conductance given by $K(T) = S\kappa(T)/L$ (W/K)
$R(T)$	electric resistance given by $R(T) = L\rho(T)/S$ (Ω)
$\langle K(T_h) \rangle$	thermal conductance averaged over a half (hot) side of a TE material (W/K)
$\langle K(T_c) \rangle$	thermal conductance averaged over a half (cold) side of a TE material (W/K)
$\langle K(T) \rangle$	thermal conductance averaged all over a TE material (W/K)
$\langle R(T_h) \rangle$	electric resistance averaged over a half (hot) side of a TE material (Ω)
$\langle R(T_c) \rangle$	electric resistance averaged over a half (cold) side of a TE material (Ω)
A_1	coefficient of $(T_z - T)$ when $\alpha(T)$ was expanded in a power series in $(T_z - T)$ (K^{-1})
A_2	coefficient of $(T_z - T)^2$ when $\alpha(T)$ was expanded in a power series in $(T_z - T)$ (K^{-2})
B_1	coefficient of $(T_z - T)$ when $\rho(T)$ was expanded in a power series in $(T_z - T)$ (K^{-1})
B_2	coefficient of $(T_z - T)^2$ when $\rho(T)$ was expanded in a power series in $(T_z - T)$ (K^{-2})
C_1	coefficient of $(T_z - T)$ when $\kappa(T)$ was expanded in a power series in $(T_z - T)$ (K^{-1})
C_2	coefficient of $(T_z - T)^2$ when $\kappa(T)$ was expanded in a power series in $(T_z - T)$ (K^{-2})
Q_h	heat energy at the hot junction of a TE element (W)
Q_c	heat energy at the cold junction of a TE element (W)
Q	difference $(Q_h - Q_c)$ in the heat energy between both end junctions of a TE element (W)
S	cross-sectional area of a TE element (m^2)
L	length of a thermoelectric material of a TE element (m)
R_L	load resistance (Ω)
I	electric current flowing through a TE element (A)

Greek letters

α	Seebeck coefficient of a TE material (V/K)
$\alpha(T_h)$	Seebeck coefficient at the hot junction of a TE element (V/K)
$\alpha(T_c)$	Seebeck coefficient at the cold junction of a TE element (V/K)
κ	thermal conductivity of a TE material (W/mK)
ρ	electrical resistivity of a TE material (Ω m)
γ	parameter defined as $(1 + ZT)^{-1/2}$
$\beta(T_h)$	Thomson coefficient at the hot junction of TE element (defined as $T_h(d\alpha/dT)$) (V/K)
$\beta(T_c)$	Thomson coefficient at the cold junction of TE element (defined as $T_c(d\alpha/dT)$) (V/K)
η	energy conversion efficiency for $B_1 \neq 0$ and $C_1 \neq 0$ K^{-1} and $A_2 \neq 0$, $B_2 \neq 0$ and $C_2 \neq 0$ K^{-2} (%)
η_0	energy conversion efficiency for $B_1 = C_1 = 0$ K^{-1} and $A_2 = B_2 = C_2 = 0$ K^{-2} (%)
η_{exp}	energy conversion efficiency obtained experimentally for a TE generator (%)
η_{the}	energy conversion efficiency estimated for a generator using the theoretical expression (%)

analytically on the assumption that the terms dependent on the temperature difference ΔT imposed on a TE element are sufficiently small compared with those independent of ΔT. It is clarified in this paper that η/η_0 of the high-performance half-Heusler compound [5] is affected significantly by the temperature dependences of TE properties. In addition, it is investigated what effect each temperature dependence of TE properties has on η/η_0.

The purpose of this paper is to investigate what effect the linear and non-linear components in the temperature dependences of α, ρ and κ of a TE material have on η of a single TE element and is to show to what degree η of a TE element is affected by the temperature dependences of TE properties.

2. Analysis

2.1. Temperature dependence of thermoelectric properties

Let us consider a single TE element in which a TE parallelepiped is welded with two electrically conducting materials, as shown in Fig. 1. When the temperature difference was imposed on a TE element, the voltage is generated between both ends of a TE element and the current flows through a circuit. The current can then be used to power a load, thus converting the thermal energy into electric energy. For a majority of cases a one-dimensional model has turned out to be sufficient to obtain quantitatively correct performance data [10]. Assuming that the temperature difference between the hot (T_h) and cold (T_c) junctions of a TE element is ΔT and the mean temperature is T, T_h and T_c are expressed as $T + \Delta T/$

2 and $T - \Delta T/2$, respectively, at least when the temperature within a TE parallelepiped changes linearly along its length direction. Thus, η should depend on the temperature dependence of the TE properties of a TE material, because generally the TE properties differ appreciably at the hot and cold junctions.

Generally, the Seebeck coefficient $\alpha(T)$, the electric resistance $R(T)$ and the thermal conductance $K(T)$ of a TE element vary with changes in temperature T over a working temperature range. The difference in α between both junctions has been taken into the conventional thermal rate equations, but the differences in R and
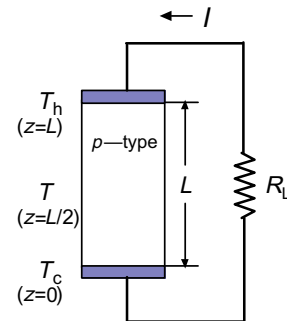

Fig. 1. A single TE element (possessing the length L and cross-sectional area S) sandwiched between two metals on which the temperature difference ΔT is imposed, where T_h and T_c are the temperatures at the hot and cold junctions, T is the mean element temperature and I is a current flowing through a circuit composed of a TE element and a load resistance R_L.

K between the hot and cold sides have always been neglected. In other words, α has been replaced with an average value $\langle\alpha\rangle$ over a working temperature range, the resistances of the hot and cold sides have been replaced by $R/2$ so that the Joule heat is divided equally into the hot and cold sides and K has been regarded as a constant throughout a TE element. However, the linear changes in α, ρ and κ with temperature were recently taken into them by us, so that it was clarified that the temperature dependence of ρ has a significant effect on η/η_0 [8]. It is thus examined here to what degree η of a single TE element is affected by the linear and non-linear components in the temperature dependences of TE properties. Here, let us assume that $\alpha(T)$, $\rho(T)$ and $\kappa(T)$ of a TE element are expressed as a quadratic function of T over a working temperature range. As described in Appendix, when the temperature within a TE parallelepiped changes linearly along its length direction (see Fig. 1), both α_h and α_c at the hot and cold junctions are expressed as

$$\alpha_h = \alpha_c = \alpha(T)[1 - (\Delta T)^2 A_2/4] \tag{1}$$

by taking the Thomson coefficients into the thermal rate equations. Subsequently, the resistances $\langle R(T_h)\rangle$ and $\langle R(T_c)\rangle$ averaged over a half (hot or cold) side of a TE parallelepiped are expressed as

$$\langle R(T_h)\rangle = (R(T)/2)[1 + (\Delta T)B_1/4 + (\Delta T)^2 B_2/12] \tag{2}$$

and

$$\langle R(T_c)\rangle = (R(T)/2)[1 - (\Delta T)B_1/4 + (\Delta T)^2 B_2/12] \tag{3}$$

as a function of ΔT (see Appendix). The conventional theory has been dealt as $B_1 = 0\ \text{K}^{-1}$ and $B_2 = 0\ \text{K}^{-2}$, but we will treat here as $B_1 \neq 0\ \text{K}^{-1}$ and $B_2 \neq 0\ \text{K}^{-2}$, because $(\Delta T)B_1/4$ and $(\Delta T)^2 B_2/12$ have values of -0.13 and 0.016 at $\Delta T = 440\ \text{K}$ in the half-Heusler compound [5], whose values are not negligibly small compared with one.

When ΔT was applied to a TE element, the thermal conductance $\langle K(T)\rangle$ averaged all over a TE parallelepiped is expressed as

$$\langle K(T)\rangle = K(T)[1 - (\Delta T)^2(C_1^2 - C_2)/12] \tag{4}$$

as described in Appendix, where $K(T) = S\kappa(T)/L$. The reason that the thermal conductance of a TE material cannot be divided into two parts of $\langle K(T_h)\rangle$ and $\langle K(T_c)\rangle$ averaged over a half side is that the continuity of heat conduction along a TE element never permits us to divide $\langle K(T)\rangle$ of a TE material into $\langle K(T_h)\rangle$ and $\langle K(T_c)\rangle$. Even though it was divided into two parts, however, the difference between $\langle K(T_h)\rangle$ and $\langle K(T_c)\rangle$ of the half-Heusler compound is small so that it is not necessary to discriminate between them, because there is little difference in κ between the hot and cold junctions. Therefore, it would be allowed to express a thermal conductance of a TE element by $\langle K(T)\rangle$ alone. In the half-Heusler compound, $(\Delta T C_1)^2/12$ and $(\Delta T)^2 C_2/12$ take values of 0.00017 and 0.044 at $\Delta T = 440\ \text{K}$, respectively. The former is much smaller than one, but the latter is not negligibly small compared with one. The whole $\langle K(T)\rangle$ of a TE material depends on the sign of C_2 but not on the sign of C_1.

As mentioned above, Eqs. (1)–(4) were derived by replacing dT_z/dz with $\Delta T/L$ on the assumption that a TE element has a linear temperature profile along its length. For this reason, these equations may be inapplicable for the practical generators which have a strong non-linearity in the temperature profile along the length. However, it is possible to derive more accurate expressions for α_h, α_c, $\langle R(T_h)\rangle$, $\langle R(T_c)\rangle$ and $\langle K(T)\rangle$ by substituting the practical tem-

perature gradient dT_z/dz into Eqs. (A.5), (A.6), (A.9), and (A.13) in Appendix.

2.2. η derived by taking into account the temperature dependence of thermoelectric properties

Here we make an attempt to take the temperature dependences of TE properties into the energy conversion efficiency η. First of all, we derive the new thermal rate equations using $\alpha(T_h)$, $\alpha(T_c)$, $\langle R(T_h)\rangle$, $\langle R(T_c)\rangle$, $\langle K(T)\rangle$, $\beta(T_h)$ and $\beta(T_c)$, where $\beta(T_h)$ and $\beta(T_c)$ are the Thomson coefficients defined as $\beta(T_h) = T_h(d\alpha/dT)$ and $\beta(T_c) = T_c(d\alpha/dT)$ [11]. When ΔT is applied to a TE element and the Seebeck and Thomson effects result in the power generation, the thermal rate equations at the hot and cold junctions for a TE element can thus be expressed as

$$Q_h = \alpha_h T_h I - \langle R(T_h)\rangle I^2 + \langle K(T)\rangle \Delta T \tag{5}$$

and

$$Q_c = \alpha_c T_c I + \langle R(T_c)\rangle I^2 + \langle K(T)\rangle \Delta T \tag{6}$$

where T is the mean TE element temperature of $(T_h + T_c)/2$, $\langle K(T)\rangle$ is the average thermal conductance of a TE material, α_h and α_c are the Seebeck coefficients at the hot and cold junctions, and Q_h and Q_c are thermal energies heated and cooled at the hot and cold junctions [12]. The first, second and third terms in both equations represent the Peltier and Thomson effects, Joule heating and thermal conduction, respectively. When $\langle R(T_h)\rangle = \langle R(T_c)\rangle = R(T)/2$ and $\langle K(T)\rangle = K(T)$, these equations correspond to the thermal equations reported by Min et al. [11] By substituting Eqs. (1)–(4) into Eqs. (5) and (6), the new thermal rate equations are expressed as

$$Q_h = \alpha(T)[1 - (\Delta T)^2 A_2/4]T_h I - R(T)[1 + (\Delta T)B_1/4 + (\Delta T)^2 B_2/12]I^2/2 + K(T)\Delta T[1 - (\Delta T)^2(C_1^2 - C_2)/12] \tag{7}$$

and

$$Q_c = \alpha(T)[1 - (\Delta T)^2 A_2/4]T_c I + R(T)[1 - (\Delta T)B_1/4 + (\Delta T)^2 B_2/12]I^2/2 + K(T)\Delta T[1 - (\Delta T)^2(C_1^2 - C_2)/12] \tag{8}$$

at least when there is no heat transfer to or from the surroundings other than a TE element. After all, the term of A_1 is canceled out by that of the Thomson coefficient, as already pointed out by Ioffe [7], so that the terms of A_2, B_1, B_2, C_1 and C_2 remain in the thermal rate equations. If these parameters are equal to zero, of course, these thermal rate equations are reduced to the conventional thermal rate equations [7]. The energy difference Q between Q_h and Q_c is given by

$$Q = Q_h - Q_c$$
$$= \alpha(T)[1 - (\Delta T)^2 A_2/4]\Delta T I - R(T)[1 + (\Delta T)^2 B_2/12]I^2 = R_L I^2 \tag{9}$$

where $R_L I^2$ is the electric energy consumed in a load resistance R_L [7]. From Eq. (9), the current I flowing through a circuit is obtained simply as

$$I = \frac{\alpha(T)[1 - (\Delta T)^2 A_2/4]\Delta T}{\{R_L + R(T)[1 + (\Delta T)^2 B_2/12]\}} \tag{10}$$

The energy conversion efficiency η of a TE element is defined as Q/Q_h [7] and is expressed as

$$\eta = \frac{R_L I^2}{\alpha(T)[1 - (\Delta T)^2 A_2/4]T_h I - R(T)[1 + (\Delta T)B_1/4 + (\Delta T)^2 B_2/12]I^2/2 + K(T)[1 - (\Delta T)^2(C_1^2 - C_2)/12]} \tag{11}$$

By substituting Eq. (10) into Eq. (11) and setting $R_L/R(T) = m$, η is rewritten as

$$\eta = \frac{a}{(b+c)} \tag{12}$$

where

$$a = Z\Delta Tm[1 - (\Delta T)^2 A_2/4]^2,$$
$$b = [1 - (\Delta T)^2(C_1^2 - C_2)/12][m + 1 + (\Delta T)^2 B_2/12]^2$$

and

$$c = Z[1 - (\Delta T)^2 A_2/4]^2[T_h(m + 1 - (\Delta T)^2 B_2/12)$$
$$- (\Delta T/2)(1 + (\Delta T)B_1/4 + (\Delta T)^2 B_2/12)]$$

where $Z = \alpha(T)^2/R(T)K(T)$. By setting $d\eta/dm = 0$, the quadratic equation of m for the maximum η is obtained as

$$(1 - m^2)[1 - (\Delta T)^2(C_1^2 - C_2)/12] + ZT - Z(\Delta T)^2 B_1/8$$
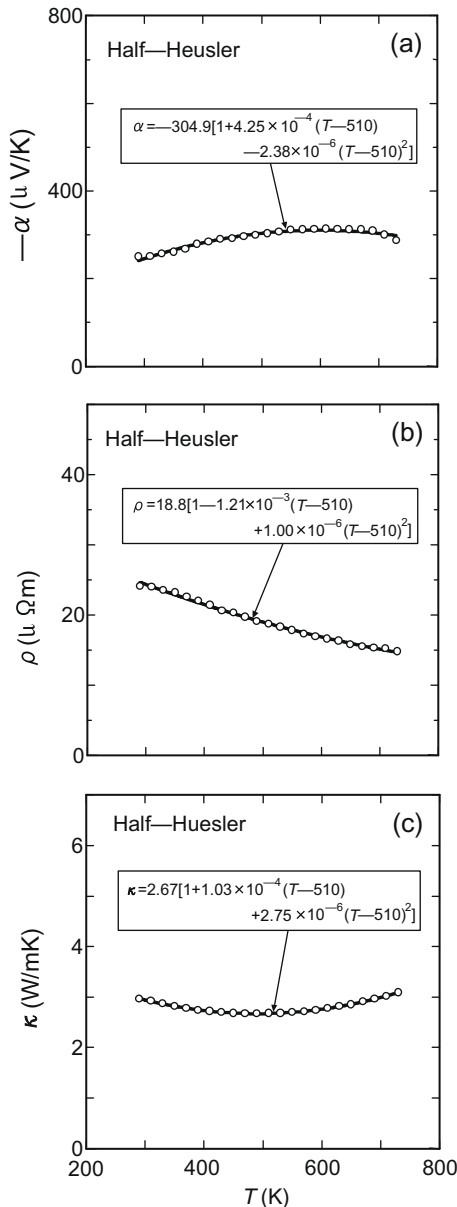$$+ (1 + ZT/2)(\Delta T)^2 B_2/6 - Z(\Delta T)^2 A_2/2 = 0 \tag{13}$$

Fig. 2. Temperature dependences of (a) α, (b) ρ and (c) κ for the n-type half-Heusler compound.

When the terms of $(\Delta T)^2$ are very small compared with one, Eq. (13) is rewritten as

$$m^2 = \gamma^{-2}\{1 + [(1 - \gamma^2)(\Delta T)^2/12][6A_2 - (3B_1/2T)$$
$$+ (1 + \gamma^2)B_2/(1 - \gamma^2) + (C_1^2 - C_2)]\} \tag{14}$$

where

$$\gamma = (1 + ZT)^{-1/2} \tag{15}$$

When the second term in the brace in Eq. (14) is very small compared with one, m is expressed approximately as

$$m = \gamma^{-1}\{1 + (1 - \gamma^2)(\Delta T)^2/24][6A_2 - (3B_1/2T)$$
$$+ (1 + \gamma^2)B_2/(1 - \gamma^2) + (C_1^2 - C_2)]\} \tag{16}$$

By substituting Eq. (16) into Eq. (12), moreover, η is expressed by a similar approximation as

$$\eta = \eta_0\left\{1 + \frac{(1+\gamma)\gamma(\Delta T)^2 T}{2(\gamma T_c + T_h)}\left[-A_2 + \frac{(1-\gamma)B_1}{4(1+\gamma)T} + \frac{(-B_2 + C_1^2 - C_2)}{6}\right]\right\} \tag{17}$$

where η_0 is the original energy conversion efficiency derived from the conventional thermal rate equations and is expressed as [7]

$$\eta_0 = \frac{(1-\gamma)\Delta T}{(\gamma T_c + T_h)} \tag{18}$$

When α, R and K are expressed by a quadratic function of T, the term of A_1 disappears but the terms of other parameters remain in η. Of course, η is reduced to η_0 for $B_1 = C_1 = 0 \text{ K}^{-1}$ and $A_2 = B_2 = C_2 = 0 \text{ K}^{-2}$. It is thus found that η/η_0 depends strongly on the sign and magnitude of parameters of A_2, B_1, B_2, C_1 and C_2. Eq. (17) is found to provide an information enough to investigate the effect of the temperature dependences of α, ρ and κ on η, although it is derived approximately from the thermal rate equations.

However, it should be noted here that even when the present approximation method is unavailable, it is possible to estimate the accurate η numerically without approximation. That is, η can be estimated exactly by substituting the value of m obtained numerically from Eq. (13) using the values of various parameters into Eq. (12).

3. Results and discussion

3.1. Parameters of A_1, A_2, B_1, B_2, C_1 and C_2 for the high-performance half-Heusler compound

Figs. 2 and 3 show the temperature dependences of α, ρ, κ and Z for the high-performance n-type $(Zr_{0.5}Hf_{0.5})Ti_{0.5}NiSn_{0.998}Sb_{0.002}$ compound [5], which has an extremely high value of $ZT = 1.50$ at 700 K. The TE properties of this compound can be expressed well by a quadratic function of $(T - 510)$, as shown in Fig. 2. T_z used in Appendix will be replaced by T hereafter, because T used until this time is replaced with a constant value of $T = 510$ K. The parameters of A_1, A_2, B_1, B_2, C_1 and C_2 which are coefficients of $(T - 510)$ and $(T - 510)^2$ were determined by the least square fitting to the experimental values of α, ρ and κ for the half-Heusler compound in the temperature range from 290 to 730 K, as listed in Table 1. In this compound, A_1, B_2, C_1 and C_2 are positive in sign but A_2 and B_1 are negative in sign. Of course, the values of these parameters would change significantly with the chemical composition of half-Heusler compounds [5,13–15]. The Z value calculated using these parameters reproduces well their experimental values, as shown in Fig. 3a. This good agreement between the experimental values and calculated curve indicates that the present approximation is valid for this half-Heusler compound employed here. The
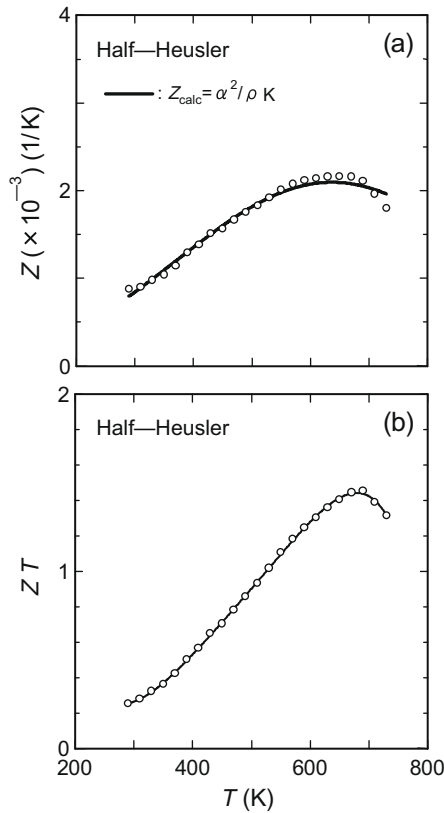
Fig. 3. Temperature dependences of Z and ZT measured for the n-type half-Heusler compound, where the solid curve of Z was drawn using the expressions obtained by the least square fitting to the temperature dependences of α, ρ and κ and that of ZT was drawn to pass through the experimental values.

Table 1
The parameters of A, B and C estimated at $T = 510$ K from the temperature dependences of the thermoelectric properties for the half-Heusler compound (Ref. [5]).

Items	Coefficient of $(T_z - T)$ (K^{-1})	Coefficient of $(T_z - T)^2$ (K^{-2})
α	$A_1 = 4.25 \times 10^{-4}$	$A_2 = -2.38 \times 10^{-6}$
ρ	$B_1 = -1.21 \times 10^{-3}$	$B_2 = 1.00 \times 10^{-6}$
κ	$C_1 = 1.03 \times 10^{-4}$	$C_2 = 2.75 \times 10^{-6}$

temperature dependences of TE properties are expressed well by a quadratic function of temperature in some high-performance TE materials; for example, $AgPb_{18}SbTe_{20}$ [8] and Bi-Te [16].

The Thomson coefficients $\beta(T_h)$ and $\beta(T_c)$ for the half-Heusler compound were calculated using the relations $\beta(T_h) = T_h(d\alpha/dT)_{T=T_h}$ and $\beta(T_c) = T_c(d\alpha/dT)_{T=T_c}$. As a result, $\beta(T_h)$ at $T_h = 730$ K and $\beta(T_c)$ at $T_c = 290$ K were 138.1 and -129.8 μV/K, respectively. Their absolute values are close to $\beta = 129$ μV/K estimated theoretically by Ioffe [7] using a non-degenerated model. It indicates that the valence band of the half-Heusler compound may indeed form a non-degenerate band.

3.2. Dependence of η/η_0 on ΔT, the values of parameters and ZT

The dependence of η/η_0 on ΔT was calculated as a function of ΔT by substituting the values of parameters (listed in Table 1) for the n-type half-Heusler compound into Eq. (17), as shown in Fig. 4. Consequently, η/η_0 increases quadratically with an increase of ΔT and reached a great value of 1.108 at $\Delta T = 440$ K. Then, the degrees of contribution from the first, second and third terms in the square bracket of Eq. (17) to η/η_0 are 0.154, -0.006 and
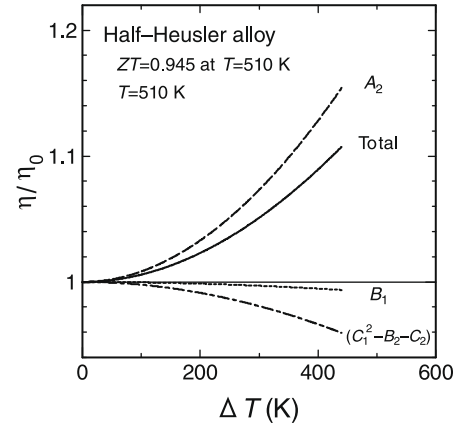

Fig. 4. (a) η/η_0 calculated as a function of $X(=B_1$ and $C_1)$ and (b) η/η_0 as a function of $X(=A_2, B_2$ and $C_2)$ under the temperature condition of $T = 510$ K and $\Delta T = 440$ K for the n-type half-Heusler compound.
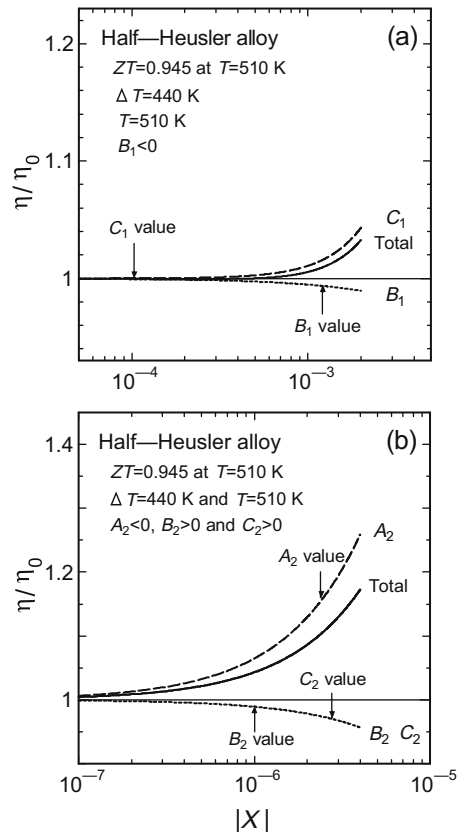

Fig. 5. η/η_0 calculated as a function of ΔT at $T = 510$ K for the n-type half-Heusler compound. The arrows in the figure denote the value of each parameter.

-0.040, respectively. It is thus found that the degree of increase in η/η_0 depends strongly on the sign and magnitude of A_2. If the values of these parameters remain unvaried with changes in ΔT, therefore, η/η_0 would be enhanced significantly with further increase in ΔT.

Next, the dependence of η/η_0 on $X(=A_2, B_1, B_2, C_1$ and $C_2)$ was calculated at $T = 510$ K as a function of X using Eq. (17) under a condition of $\Delta T = 440$ K for the half-Heusler compound [5] and drawn as a function of X in Fig. 5. As evident from Eq. (17), η/η_0 changes linearly with an increase of A_2, B_1, B_2 and C_2 but increases quadratically with an increase of C_1, so that the dependences of η/η_0 on the

parameters change entirely according to their sign and magnitude. It is seen from the figure that η/η_0 varies significantly with changes in A_2, particularly at large ΔT, as mentioned above. The sign and magnitude of A_2 have a much more significant effect on η/η_0 than those of other parameters. The error due to the approximation for the increment $(\eta/\eta_0 - 1)$ in η/η_0 is about 6% at $\Delta T = 440$ K, so that Eq. (17) is found to hold well even for a great temperature difference of $\Delta T = 440$ K. Therefore, the present results would be almost unvaried basically even if η/η_0 was derived numerically or exactly from Eqs. (12) and (13).

Subsequently, η and η_0 were calculated at $T = 510$ K as a function of ZT for $\Delta T = 440$ K and their curves were drawn as a function of ZT in the range from $ZT = 0$ to 3 in Fig. 6a, where η was calculated from Eq. (17) using the parameters listed in Table 1. Here the change in ZT means a change in Z. Both η and η_0 tend to increase monotonically with an increase of ZT. η is somewhat higher than η_0 all over the range. Under the condition of $T = 510$ K and $\Delta T = 440$ K, however, η is approximately 11% at $ZT = 0.945$ higher than η_0 in the half-Heusler compound. However, η/η_0 tends to decrease slightly with an increase of ZT, as shown in Fig. 6b. In any case, the fact that η is larger than η_0 indicates that when one evaluates the accurate achievement rate of η_{exp} obtained experimentally for a TE generator, therefore, η_{exp} should be compared with η_{the} estimated theoretically from Eq. (17), not with the conventional η_0.

The estimation of η/η_0 using the temperature dependences of the TE properties evaluated at the average temperature T would thus provide the exact results, at least as long as the temperature dependence of TE properties was expressed as a quadratic function of temperature and the real temperature gradient dT_z/dz was employed. Here the real dT_z/dz corresponds to the temperature gradient of the temperature distribution obtained by the least square fitting of a polynomial to the practical temperature profile of a TE element.
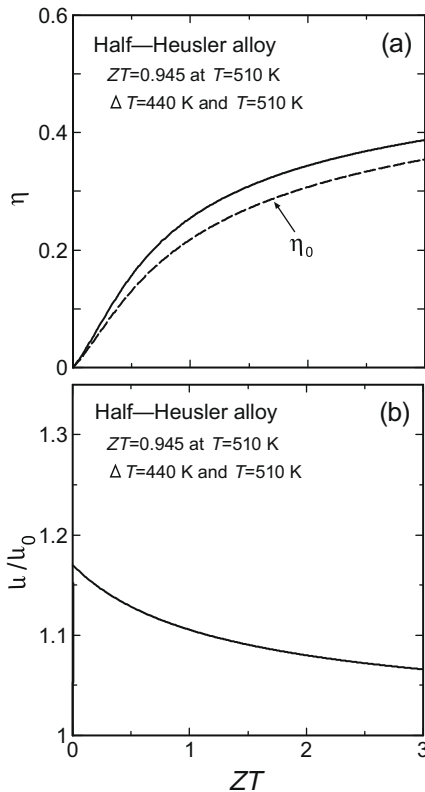
3.3. $Z_{eff}T$ obtained by ascribing the increase in η/η_0 to the increase in the intrinsic ZT

The effective $Z_{eff}T$ for a TE element was calculated by ascribing the increase in η/η_0 due to the parameters of A_2, B_1, B_2, C_1 and C_2 to the increase in the intrinsic ZT. For simplicity, Eq. (17) is rewritten as

$$\frac{\eta}{\eta_0} = 1 + Y \tag{19}$$

where

$$Y = \frac{\gamma(1+\gamma)(\Delta T)^2 T}{2(\gamma T_c + T_h)}\left[-A_2 + \frac{(1-\gamma)B_1}{4(1+\gamma)} + \frac{(-B_2 + C_1^2 - C_2)}{6}\right] \tag{20}$$

where $\gamma = (1 + ZT)^{-1/2}$. If we attribute this increase in η/η_0 to the increase in the intrinsic ZT, η is expressed as

$$\eta = \frac{(1 - \gamma_{eff})\Delta T}{(\gamma_{eff} T_c + T_h)} \tag{21}$$

using the effective $\gamma_{eff} = (1 + Z_{eff}T)^{-1/2}$. Substituting Eqs. (18) and (21) into Eq. (19), γ_{eff} is expressed as

$$\gamma_{eff} = \gamma - \frac{(1-\gamma)(\gamma T_c + T_h)Y}{2T} \tag{22}$$

Substituting Eq. (20) into Eq. (22), the effective $Z_{eff}T$ is expressed approximately as

$$Z_{eff}T = ZT\left\{1 + \frac{(\Delta T)^2}{2}\left[-A_2 + \frac{(1-\gamma)B_1}{4(1+\gamma)T} + \frac{(C_1^2 - B_2 - C_2)}{6}\right]\right\} \tag{23}$$

Fig. 6. (a) η and (b) η/η_0 calculated at $T = 510$ K as a function of ZT under a temperature difference of $\Delta T = 440$ K for the n-type half-Heusler compound.
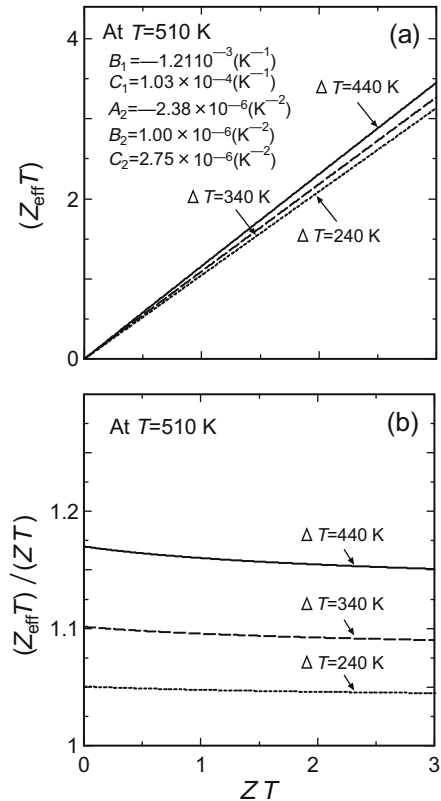

Fig. 7. (a) The effective $(Z_{eff}T)$ calculated at $T = 510$ K as a function of the intrinsic ZT using Eq. (23) by ascribing the increase in η due to the parameters to the increase in the intrinsic ZT and (b) $(Z_{eff}T)/(ZT)$ calculated as a function of the intrinsic ZT using Eq. (23).

using the intrinsic ZT, A_2, B_1, B_2, C_1 and C_2. This expression shows that $Z_{eff}T$ becomes larger or smaller than the intrinsic ZT according to the sign and magnitude of A_2, B_1, B_2, C_1 and C_2. In order to investigate the effect of the increase in η/η_0 due to these parameters on $Z_{eff}T$, therefore, $Z_{eff}T$ and $Z_{eff}T/ZT$ were calculated as a function of ZT at $T = 510$ K by substituting these parameters (listed in Table 1) into Eq. (23) under the conditions of $\Delta T = 240$, 340 and 440 K. Of course, $Z_{eff}T$ is well-defined by Eq. (23) even at $\Delta T = 440$ K, because the approximation used in deriving Eq. (17) holds well even for a large value of $\Delta T = 440$ K, as mentioned earlier. As shown in Fig. 7a, $Z_{eff}T$ increases almost linearly with an increase of ZT and the gradient tends to increase with an increase of ΔT. The ratio of $(Z_{eff}T)$ to (ZT) is enhanced significantly at larger ΔT, but it tends to decrease slightly and almost linearly with an increase of ZT, as shown in Fig. 7b. The ratio reached a great value of 1.16 at $ZT = 0.945$ under the condition of $T = 510$ K and $\Delta T = 440$ K. It indicates that $Z_{eff}T$ of a TE element is enhanced significantly even by the temperature dependences of TE properties. It was thus found that the temperature dependences of TE properties have a significant influence on the energy conversion efficiency η of a TE element, particularly at large ΔT.

4. Conclusions

The new thermal rate equations were built up by introducing both the linear and non-linear components in the temperature dependences of α, ρ and κ of a TE material on the assumption that they are expressed as a quadratic function of temperature. The differences in α and ρ between the hot and cold junctions of a TE element were then taken into the thermal rate equations. The term of A_1 (coefficient of the linear temperature dependence of α) disappears but the terms of other parameters (A_2, B_1, B_2, C_1 and C_2) remain in the thermal rate equations. Of course, when $B_1 = C_1 = 0$ K^{-1} and $A_2 = B_2 = C_2 = 0$ K^{-2}, the new thermal rate equations are reduced to the conventional thermal rate ones. η/η_0 for a single TE element were calculated as functions of ΔT, X and ZT using the new thermal rate equations, where $X = A_2$, B_1, B_2, C_1 and C_2. Among the temperature dependences of TE properties, the non-linear component (A_2) in the temperature dependence of α has the strongest effect on η/η_0, so that the degree of increase in η/η_0 of the half-Heusler compound reached 11% under the condition of $T = 510$ K and $\Delta T = 440$ K. When one ascribed this increase in η/η_0 due to A_2, B_1, B_2, C_1 and C_2 to the increase in the intrinsic ZT, the effective $Z_{eff}T$ of the half-Heusler compound was found to be approximately 16% at $ZT = 0.945$ higher than the intrinsic ZT under the condition of $T = 510$ K and $\Delta T = 440$ K. It was clarified that the energy conversion efficiency depends strongly on the temperature dependences of α, ρ and κ.

When one evaluates the accurate achievement rate of η_{exp} obtained experimentally for a TE generator, therefore, η_{exp} should be compared with η_{the} estimated theoretically from Eq. (17), not with the conventional η_0.

Appendix A

Let us assume that the Seebeck coefficient α, the electric resistance R and the thermal conduction K of a TE parallelepiped increase or decrease linearly with an increase of T. Here we will show that $\langle R(T_h) \rangle$ or $\langle R(T_c) \rangle$ averaged over a half (hot or cold) side of a TE parallelepiped with length L and the resultant $\langle K(T) \rangle$ averaged all over a TE parallelepiped are expressed as a function of ΔT. When we assume that the temperature in a TE parallelepiped changes linearly with z along its length direction, as shown in Fig. 1, the temperature T_z at a position z is expressed as

$$T_z = T + (z - L/2)\Delta T/L \tag{A.1}$$

When the Seebeck coefficient α changes linearly with T, $\alpha(T_z)$ at T_z is then expressed as

$$\alpha(T_z) = \alpha(T)[1 + (T_z - T)A_1 + (T_z - T)^2 A_2] \tag{A.2}$$

where $A_1 = (d\alpha(T_z)/dT_z)/\alpha(T)$ and $A_2 = (d^2\alpha(T_z)/dT_z^2)/2\alpha(T)$. As shown in Subsection 2.1, α_h and α_c at the hot and cold junctions are expressed as

$$\alpha_h = \alpha(T_h) - \beta(T_h)\Delta T/(2T_h) \tag{A.3}$$

and

$$\alpha_c = \alpha(T_c) + \beta(T_c)\Delta T/(2T_c) \tag{A.4}$$

where $\beta(T_h)$ and $\beta(T_c)$ are the Thomson coefficients defined by the following expressions:

$$\beta(T_h) = T_h[d\alpha(T_z)/dT_z]_{T_z=T_h} = T_h[(d\alpha(T_z)/dz)/(dT_z/z)]_{z=L}$$
$$= T_h(A_1 + \Delta T A_2)\alpha(T) \tag{A.5}$$

and

$$\beta(T_c) = T_c[d\alpha(T_z)/dT_z]_{T_z=T_c} = T_c[(d\alpha(T_z)/dz)/(dT_z/z)]_{z=0}$$
$$= T_c(A_1 - \Delta T A_2)\alpha(T) \tag{A.6}$$

Substituting Eq. (A.2) into Eqs. (A.3)–(A.6), the term of A_1 disappears in their equations but that of A_2 remains so that both α_h and α_c are rewritten as

$$\alpha_h = \alpha_c = \alpha(T)[1 - (\Delta T)^2 A_2/4] \tag{A.7}$$

It is thus found that the relation $\alpha_h = \alpha_c$ holds even for $A_2 \neq 0$ K^{-2} in the present approximation.

Subsequently, when the electrical resistivity ρ changes linearly with T, $\rho(T_z)$ at T_z is then expressed as

$$\rho(T_z) = \rho(T)[1 + (T_z - T)B_1 + (T_z - T)^2 B_2] \tag{A.8}$$

Therefore, the average $\langle R(T_h) \rangle$ of the upper (hot) side (corresponding to a half of a TE parallelepiped) is given by

$$\langle R(T_h) \rangle = \int_{L/2}^{L} \frac{\rho(T_z)}{S} dz = \int_{T}^{T_h} \frac{\rho(T_z)}{S} \frac{dz}{dt_z} dT_z \tag{A.9}$$

Using the relation $dT_z/dz = \Delta T/L$, $\langle R(T_h) \rangle$ is obtained as

$$\langle R(T_h) \rangle = (R(T)/2)(1 + (\Delta T)B_1/4 + (\Delta T)^2 B_2/12) \tag{A.10}$$

In the same way, the average $\langle R(T_c) \rangle$ is also derived as

$$\langle R(T_c) \rangle = (R(T)/2)(1 - (\Delta T)B_1/4 + (\Delta T)^2 B_2/12) \tag{A.11}$$

Moreover, if the thermal conductivity κ changes linearly with temperature, $\kappa(T_z)$ at T_z is then expressed as

$$\kappa(T_z) = \kappa(T)[1 + (T_z - T)C_1 + (T_z - T)^2 C_2] \tag{A.12}$$

When there is a temperature difference ΔT along a TE element, therefore, the resultant $\langle K(T) \rangle$ of a TE parallelepiped is given by

$$\frac{1}{\langle K(T) \rangle} = \frac{1}{S}\int_0^L \frac{1}{\kappa(T)_z}dz = \frac{1}{S}\int_{T_c}^{T_h} \frac{1}{\kappa(T_z)}\frac{dz}{dt_z}dT_z \tag{A.13}$$

$$= \frac{L}{S\kappa(T)\Delta T}\int_{-|\Delta T/2|}^{\Delta T/2} \frac{dx}{(1 + xC_1 + x^2 C_2)}$$
$$= \frac{L}{2C_2 S\kappa(T)\Delta T Ai}\{\ln|[1 + \Delta T/(C_1/C_2 - 2Ai)]/[1 - \Delta T/(C_1/C_2 - 2Ai)]|$$
$$- \ln|[1 + \Delta T/(C_1/C_2 + 2Ai)]/[1 - \Delta T/C_1/C_2 + 2Ai)]|\} \tag{A.14}$$

where $A = (1 - C_1^2/4C_2)^{1/2}$ and i denotes the imaginary number. When $|\Delta T/(C_1/C_2 + 2Ai)| \ll 1$ and $|\Delta T/(C_1/C_2 - 2Ai)| \ll 1$, $1/\langle K(T) \rangle$ is expanded in a power series in ΔT and the resultant $\langle K(T) \rangle$ is expressed as

$$\langle K(T)\rangle = K(T)[1 - (\Delta T)^2(C_1^2 - C_2)/12] \tag{A.15}$$

where $K(T) = S\kappa(T)/L$.

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